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THE TEMPERATURE DISPERSOIN OF COMPLEX DIELECTRIC CONSTANT OF DIPOLAR LIQUIDS IN THE MICROWAVE REGION λ=3. 2cm (9375 Mc/s)*

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Özet

Bu çalışmada 3,2 cm dalga boylu (9375 Mc/s) mikrodalgaların girişimi metodu ile bazı dipollü sıvıların ε' dielektrik sabitleri ve ε'' dilektrik kayıp faktörlerinin sıcaklık dispersiyonu incelenmiştir.

Bromoform, anilin, o–kloro–anilin ile bromosikloheksanın dielektik kayıp faktörleri belirli sıcaklıklarda birer maksimum göstermişlerdir. ε''nün maksimum değeri ile ε'nün karşıt değerlerini kullanarak ε_∞ optik dielektrik sabitlerini hesaplamak mümkün oldu ve bromofrom, anilin ve–o–kloro–anilin için n kırılma indisinin karesinden büyük olduğu bulundu. Bunun atomik polarizasycndan ileri geldiği anlaşılmaktadır. Buna göre bromosikloheksan halinde ε_∞, n^2 ye eşit olduğundan bu sıvının moleküllerinin atomik polarizasyona uğramadığı anlaşıldı.

Çalışmada bundan başka dipollü sıvıkların atomik polarizasyonlarını tayin etmenin mümkün olduğu gösterildi.

Summary

We have investigated the temperature disperison of dielectric constants and dielectric loss factors of some dipolar liquids with the microwave interference method at 3.2 cm · (9375 Mc/s).

The imaginary part ε'' of the complex dielectric constant of bromoform, aniline, o–chloro–aniline and bromocyclohexane

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exibit maximums at certain temperatures. Using the measured maximum value of ε'' and the corresponding value of ε' it has been possible to calculate ε_∞ the optical dielectric constant, and it has been found that for bromoform, aniline and o–chloro–aniline it is larger than the square of the index of refraction. Obviouslly, this is due to the atomic polarization. In the case of bromocyclohexane ε_∞ is equal to n^2 meaning that there is no atomic polarization in the molecules of this liquid.

It has also been possible to determine the atomic polariza-tion of dipolar liquids.

Finally, I wish to express my gratitudes to Prof. R. Nasuh-oğlu for his suggestion and guidence at this work.

INTRODUCTION

Dieletic Loses and Relaxation Time.

In a static field the total polarization of a dielectric conta-ining electric dipoles is given [1] by

$$Ps = Pe + Pa + Pd \qquad (1)$$

in wich Pe, Pa and Pd are respectivly electronic, atomic, and dipolar polarizations. In general, when such a substance is suddenly exposed to an external static field, a certain lenght of time is required for Ps to be built up to its final value. Since Pe and Pa could be assumed as time independent for frequencies appreciably smaller than infrared frequecies, the built–up time for Ps, could be accepted as time in which Pd would reach its saturation value.

In order to be able to understand the behavior of dipolar liquids a phenomenological relaxation time τ is defiend by

$$\frac{dP_d(t)}{dt} = \frac{1}{\tau} (P_{ds} - P_d(t)) \qquad (2)$$

in which Pds is the saturation value of Pd. In the case of an alternating field $E = E_o e^{iwt}$ the differential equation (2) is written in the from,

$$\frac{dP_d\,(t)}{dt} = \frac{1}{\tau}\,(P_{ds}\,(t) - P_d) \qquad (3)$$

On the other hand, the *instantaneous dieletric constant* ε_{ea} is defined by

$$P_e + P_a = \frac{\varepsilon_{ea}-1}{4\pi}\,E \qquad (4)$$

and the static dielectric constant ε_s by

$$P_s = \frac{\varepsilon_s-1}{4\pi}\,E \qquad (4)$$

Taking into account the relation (1) the differential equation (3) can be put in the following form,

$$\frac{d}{dt}\,P_d(t) = \frac{1}{\tau}\,\left(\frac{\varepsilon_s - \varepsilon_{ea}}{4\pi}\,E_o\,e^{iwt} - P_d\right) \qquad (5)$$

The solution of which is

$$P_d\,(t) = Ce^{-\frac{t}{\tau}} + \frac{1}{4\pi}\,\frac{\varepsilon_o-\varepsilon_{ea}}{1+iw}\,E_o\,e^{iwt} \qquad (6)$$

where the first term represents a transient which will be zero after a certain time.

On the other hand between the displacement D, the electric fiel E and the polarization P there is the relation

$$D = \varepsilon^*\,E + 4\pi\,P \qquad (7)$$

where ε^* is the complex dielectric constant and is defined as $\varepsilon^* = \varepsilon' - j\,\varepsilon''$.

From the last two equations we can derive the following expressions:

$$\varepsilon'\,(w)\; =\; \varepsilon_{ca}\; +\; \frac{\varepsilon_s\; -\; \varepsilon_{ca}}{1\; +\; w^2\;\tau^2} \tag{8}$$

$$\varepsilon''\,(w)\; =\; (\varepsilon_s\; -\; \varepsilon_{ca})\;\frac{w\;\tau}{1\; +\; w^2\;\tau^2} \tag{9}$$

Which are referred to as the Debye [1] equations.

When $\omega\,\tau\, =\, 1$, ε'' exibits a maximum and its value is

$$\varepsilon''_m\; =\; \frac{\varepsilon_s\; -\; \varepsilon_{ca}}{2} \tag{10 a}$$

If the maximum value of ε'' is obtained by making $\omega\tau = 1$ either changing ω or τ we can callculate ε_{ca} from (10 a). For $\omega\,\tau\, =\, 1$, ε' takes the value

$$\varepsilon'_m\; =\; \frac{\varepsilon_s\; +\; \varepsilon_{ca}}{2} \tag{10 b}$$

Since in the microvawe range it is impossible to have a continuous variation of frequency the best way of the determination of ε''_m is to look to the variation of τ by temperature according to the relation $\tau\, =\,\tau_{\infty}\, e^{E/kT}$ and get the condition $\omega\,\tau = 1$ fulfilled. From equation (8) and (9) we get

$$\frac{\varepsilon''}{\varepsilon'-\varepsilon_{ca}}\; =\;\omega\,\tau \tag{11}$$

and for $\omega\tau\, =\, 1$ we can obviously get

$$\varepsilon_{ca}\; =\;\varepsilon'_m\; -\;\varepsilon''_m \tag{13}$$

The static molar polarization π_s [2] is given by

$$\pi_s\; =\;\frac{\varepsilon_s\, -\, 1}{\varepsilon_s\, +2}\;\cdot\;\frac{M}{d} \tag{14}$$

and electronic molar polarization π_e by

$$\pi_e = \frac{n^2-1}{n^2+2} \cdot \frac{M}{d} \tag{15}$$

in which $\dfrac{M}{d}$ and n are the molar volume and index of refraction respectively.

In the same way for ε_{ea} we can define an electronic and atomic polarization by

$$\pi_{ea} = \frac{\varepsilon_{ea}-1}{\varepsilon_{ea}+2} \cdot \frac{M}{d} \tag{16}$$

Generally π_s can be expressed as the sum of π_d π_a and π_e i. a.

$$\pi_s = \pi_d + \pi_a + \pi_e \tag{17}$$

where π_a is the atomic polarization.

By the same reasoning, for ε_{ea} the following expression can be written.

$$\pi_{ea} = \pi_a + \pi_e \tag{18}$$

Hence, if the index of refraction n and the instantaneous dielectric constant ε_{ea} are known it is possible to calculate π_a.

Apparatus

The block diagram of the measuring system is given in Fig.–1. It consists of a double arm microwave interferometer set up veritically. On one of the arms there are a variable phase shifter and a variable attenuator. On the other arm there is the sample holder which is inserted between two fixed attenuators of 10 db each to prevent unwanted reflexions.

The phase calibrations of the phase shifter and variable attenuator have been carried out with a variable short circuit element and a voltage standing wave ratio indicator.

The attenuator was calibrated by its maker. A null detector has been used to detect the node at A of Fig. – 1.
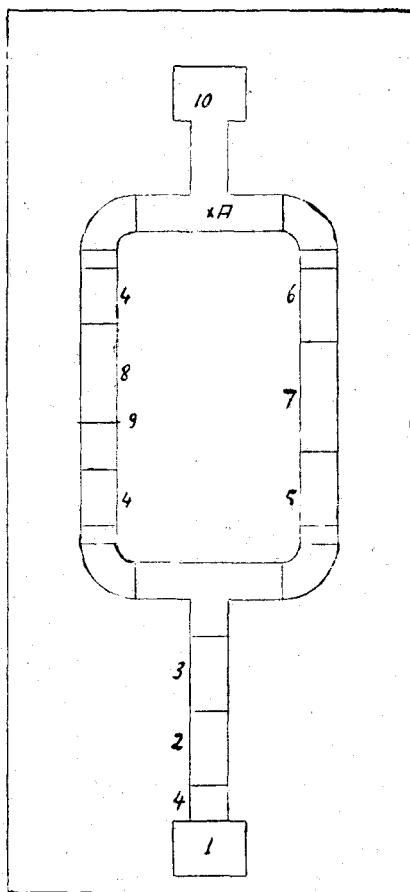
Fig. 1. The block diagram of the measuring apparatus. 1) 2K25 klystron and power unit, 2) frequencymeter, 3) magic T, 4) fixed attenuator of 10 db, 5) fixed attenuator of 20 db, 6) variable attenuator of 40 db,)7) phase shifter, 8) sample holder, 9) thin mica window, 10) null detector.

The phase shift and the attenuation caused by an increase Δl of sample thickness were determined by obtaining minimum outputs for two different quantity of the sample.

Phase factor β and attenuation factor α of a dielectric in the waveguide can be calculated by the formulae

$$\beta = \frac{\Delta\varphi}{\Delta l} + \frac{2\pi}{\lambda g}, \quad \alpha = \frac{\Delta a}{\Delta l} \quad (19)$$

in which $\Delta\varphi$ is the plase shift for Δl, λg is the wavelength in empty waveguide and Δa is the amount of attenuation for Δl.

The real and imaginary parts of the complex dielectric constant in terms of α and β are given [2] by

$$\varepsilon' = \lambda^2_o \left(\frac{2}{\lambda_c^2} + \frac{\beta^2 - \alpha^2}{4\pi^2} \right) \quad (20)$$

and

$$\varepsilon'' = \frac{\lambda^2_o \, \alpha \, \beta}{2\pi^2} \quad (21)$$

where λ_o and λ_c are free space and cut–off wavelenght respectivly.

Experimental Results

According to the relations (19) $\Delta\varphi$ and Δa are proportional to Δl. The graphes for the data on n–propyle alcohol (Fig. – 2) show the expected linearity.

In order to get rid of the unwanted reflexions on the sample surfaces a quantity of sample of 20db at least is used in measrurements.

The experimental results for n–propyl alcohol and n–butyl alcohol are given in tables 1 and 2 which are consistent with the values given in the literature and reproduced in tables 1 and 2.
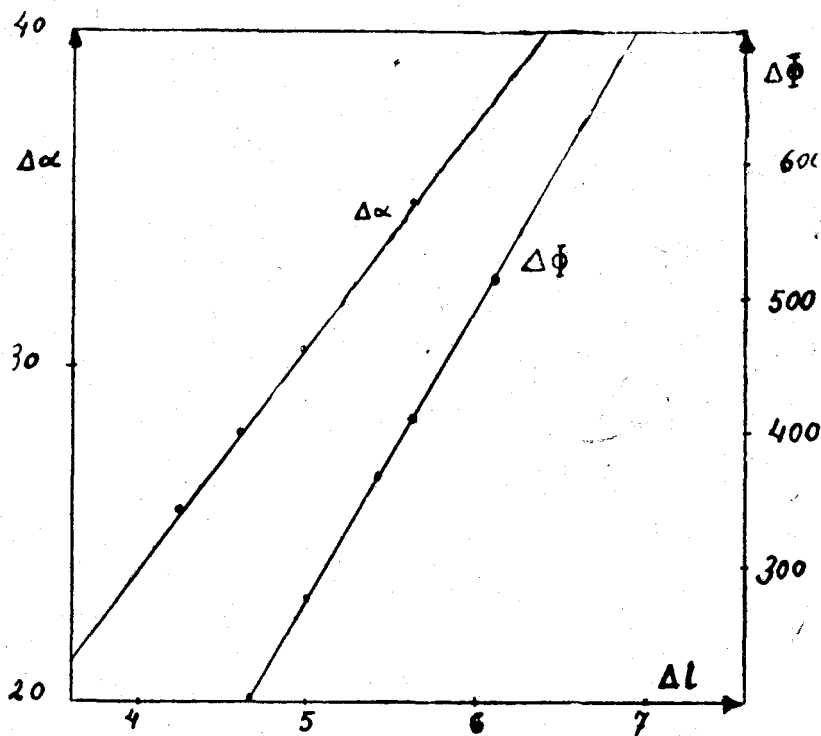
Fig. 2. The plot of $\Delta\varphi$ and Δl against Δl.

Table 1: n–Butyl alcohol

t°C	λ_0	ε'	ε''		
12	3.20	3.21	0.69		
15	..	3.19	0.69		
20	..	3.20	0.72		
25	..	3.20	0.78		
30	..	3.20	0.87		
35	..	3.19	0.95		
40	..	3.18	1.15		
25	3.24	3.08	1.08	Yosumi	[3]
5	3.08	3.05	0.67	Koizumi	[4]
20	..	3.10	0.81	..	
35	..	3.19	1.17	..	
50	..	3.35	1.35	..	
25	3.00	3.04	0.64	Crouch	[5]

Table 2: n–Propyl alcohol

t°C	λ_o	ε'	ε''	
30	3.20	3.65	1.42	
35	..	3.63	1.53	
40	..	3.57	1.74	
5	3.08	3.42	1.06	Koisumi [4]
20	..	3.45	1.30	..
35	..	3.50	1.72	..
50	..	3.61	2.36	..
20	3.45	3.62		Girard [6]
20	2.94	3.46		..

Bromofrom CHBr₃ Aniline C₆H₅NH₂ and o–chloro–aniline Cl C₆H₄NH₂

The experimental results for bromoform, aniline and o–chloro – aniline are given in table 3, 4 and 5 and plotted in Fig.–3.
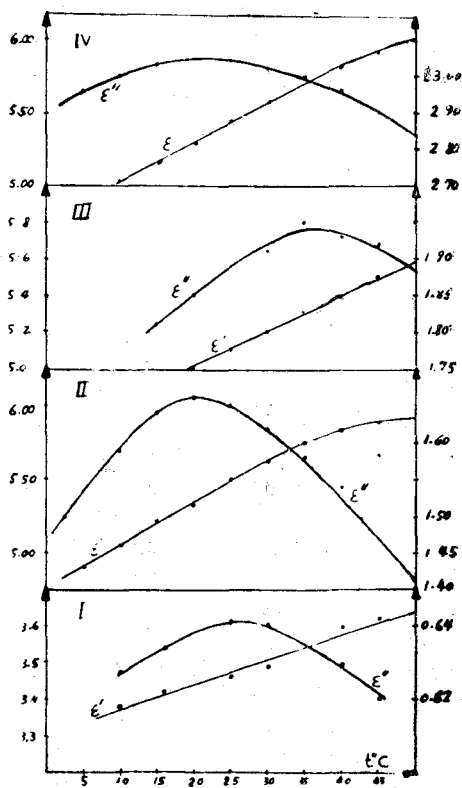

Fig. 3. The dispersion curves for bromoform (I), aniline (II), o–chloro–aniline (LIII), and bromocylohexane (IV).

Table 3 : Bromoform

t°C	ε'	ε''	ε_s	ε_{ea}	n^2	λ_k cm
7	3.375	0.625				
8	3.368	0.628				
10	3.384	0.627				
16	3.425	0.634				
25	3.465	0.642	4.33	2.823	2.55	3.2
30	3.490	0.641				
35	3.544	0.635				
40	3.599	0.629				
45	3.626	0.620				
50	3.645	0.602				

Table 4: Aniline

t°C	ε'	ε''	ε_s	ε_{ea}	n^2	λ_k cm
3	4.91	1.50				
5	4.86	1.53				
10	5.05	1.59				
15	5.23	1.64				
20	5.32	1.66	6.89	3.66	2.52	3.2
25	5.50	1.65				
30	5.62	1.62				
35	5.75	1.58				
40	5.82	1.54				
45	5.88	1.44				
50	5.93	1.37				

Table 5 : o–chloro aniline

t°C	ε'	ε''	ε_s	ε_{ea}	n^2	λ_k cm
15	4.91	1.81				
20	5.01	1.85				
25	5.10	1.89				
30	5.20	1.91				
35	5.31	1.95				
36	5.31	1.94	7.50	3.37	2.50	3.2
40	5.39	1.93				
45	5.49	1.92				
50	5.58	1.88				
55	5.65	1.86				

For each of these liquids ε' increases linearly with temperature but ε'' reveal maxima at certain temperatutures. This means that the condition $\omega \tau = 1$ is fulfiled at these temperatures.

From 13, 10 a and 10 b the following values for ε'_m and ε''_m has been calculated.

	ε'_m	ε''_m
Bromoform	3.56 ∓ 0.1	0.70 ∓ 0.05
Aniline	5.275	1.675
o–cloro–aniline	5.43	2.065

These cvalues are equal to the experimental results within the estimated errors.

As the xperimentaly deretmined values of ε_{ea} are larger than n^2 respectivly, the differences haveto be considered due to the atomic polarization.

From (15) and (18) one gets

	π_a CGS	π_e CGS
Bromofrom	3.05	29.6
Aniline	12.2	30.6

For aniline the critical wavelength λ_k corresponding to ω_k which is the value of ω that fulfils the $\omega \tau = 1$ condition, was found by Fisher [7] $\lambda_k = 3.7$ cm as a result of his measurements at $\lambda = 60.3$ cm which is close to our value $\lambda_k = 3.2$ cm.

Bromoyclohexane $C_6 H_{11} Br$

The experimental deta for bromocyclohexane are given in table 6 and Fig. 4.

ε' increases with the tempereture but ε'' exibits a maximum at 21° C.

From 13, 10 a and 10b, $\varepsilon_{ac} = 2.28$, $\varepsilon'_m = 5.16$ and $\varepsilon''_m = 2.88$ have been calculated. These values are equal to the experimental results within the experimental error.
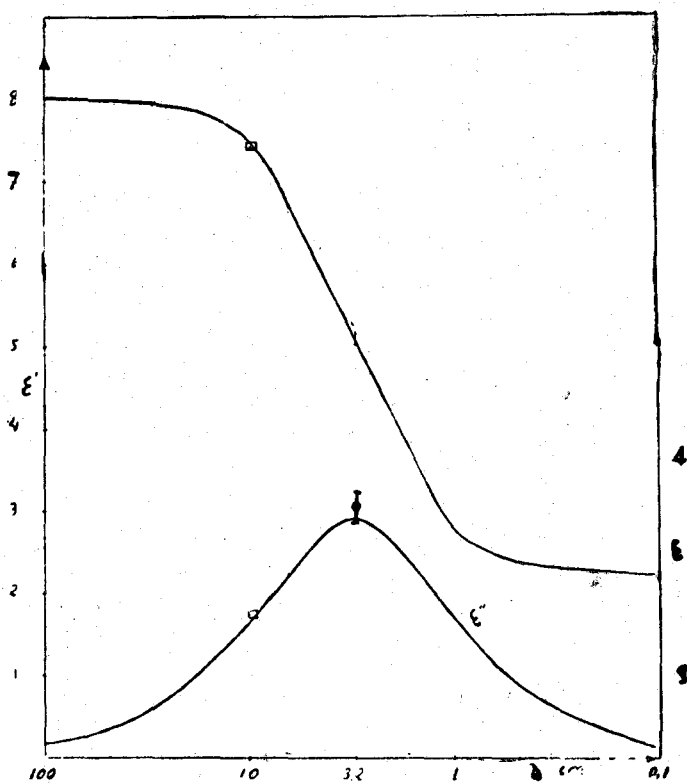
Fig. 4. Debye curves for bromocyclohexane, Φ ours, ☐ Smyth's.

Table 6 : Bromocyclohexane

t°C	ε'	ε''	ε_s	ε_{ea}	π^2	λ_k cm
5	4.89	2.96				
10	5.03	3.00				
15	5.16	3.03				
20	5.29	3.04				
21.	5.32	3.04	8.04	2.28	2.24	3.2
25	5.43	3.04				
30	5.57	3.02				
35	5.69	3.00				
40	5.81	2.96				
45	5.91	2.90				
50	5.99	2.84				
55	6.04	2.72				

The maximum of ε'' shows that the ciritical wavelength for bromocyclohexane is 3.2 cm. Dieringer [8] and Smyth [9] have found $\lambda_k = 4.7$ and $\lambda_k = 3.67$ respectively. Both of them are larger than ours.

ε_{ea} is equal to π^2 meaning that there is no atomic polarization in the molecules of this liquid.

Taking $\varepsilon_{ea} = n^2 = 2.24$ a plot of Debye curves is given in Fig 4 on which all the expeimetal points fit very well.

Conclusions

In order to describe the behavior of the dipolar dielectrics by Deby equations at high frequencies it is necessary to determine ε_{ea} and λ_k experimentally. By varying the temperature, it is possible to get the maximum of ε'' and this allows us to determine ε_{ea} and λ_k.

For bromoform, aniline and o–chloro–aniline we have found that $\varepsilon_{ea} > n^2$ which can be interpreted as a result of atomic polarization. In the case of bromocyclohexane ε_{ea} is equal to n^2 which means that there is no atomic polarization in its molecules.

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